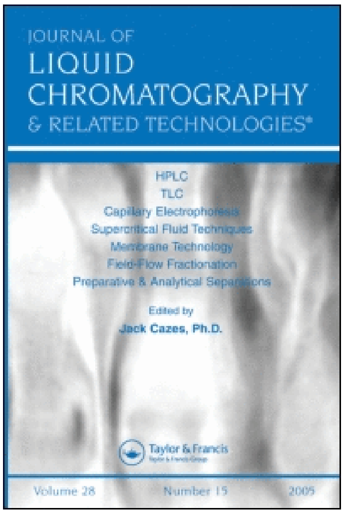

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Characterization of Sulphides by Gravitational Field-Flow Fractionation

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CHARACTERIZATION OF SULPHIDES BY GRAVITATIONAL FIELD-FLOW FRACTIONATION

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ABSTRACT

Various sulphides of the type $Cu_xZn_{(1-x)}S$ $(0<x<1)$ were characterized in terms of particle size distribution by the gravitational field-flow fractionation technique. From the variation of the number average and weight average particle diameter with various parameters, such as solution pH and ionic strength, kind of detergent and time, in combination with microelectrophoretic measurements, useful conclusions about the stability and consequently the aggregation and deposition phenomena of these sulphides were deduced.

Comparison of the results obtained by gravitational field-flow fractionation with those found by laser particle size measurements confirmed the credibility of the method used.

INTRODUCTION

Chemical precipitation of heavy metals, which are of the most hazardous in the natural environment, is an effective process for the removal of these metals. This precipitation involves spontaneous precipitation of various salts, such as carbonates and sulphides.[1] The precipitation of heavy metals as sulphides, has the advantage of effectively removing heavy metals even at very low concentrations, owing to the low solubility of their sulphides.

Several stability studies have been performed on sulphides, stimulated by the needs of metal pollutant precipitation,[2] of mineral flotation,[3] and of sedimentation of sulphide phosphorus for cathode-ray tubes.[4] However the chemistry of the sulphide-electrolyte interface is much less known than the chemistry of the oxide-water interface. Hence there is a need not only to study the stability of the sulphides at various experimental conditions, but also to develop new methodologies for the characterization of metal sulphides.

One of the most important parameters for studying colloid's stability and deposition on solid surfaces, is the particle size distribution. In this work the relatively new technique of Gravitational Field-Flow Fractionation (GFFF) was used for the size determination of metal sulphide particles.

Field-flow fractionation (FFF) is a powerful, high-resolution separation method, which can be also used for the characterization of a wide variety of colloids, micelles, particulates and soluble macromolecules of biological interest.[5-9]

FFF is based on the action of an external field or gradient whose direction is perpendicular to the axis of flow in a thin channel. The field forces the sample species to accumulate in narrow zones so that each is intercepted by different flow laminae and thus displaced at different velocities down the flow channel. Different FFF methods are distinguished according to the nature of the external field used. In sedimentation FFF (SdFFF), a subtechnique of FFF, retention volume increases with particle diameter until steric effects dominate, at which transition point there is a foldback in elution order. The larger particles tend to move more quickly than the smaller ones in steric or gravitational FFF, and the separation mechanism is based more on inherent particle size than on the ability of a particle to undergo Brownian diffusion.[10] Gravitational FFF, which utilizes the Earth's gravitational field as an external field, has been applied to the rapid separation and/or characterization of various kinds of colloids, e.g. glass beads,[11] polystyrene latex beads[12] strengite and silica particles,[13,14] red blood cells,[15] etc.

In the present work GFFF is applied for the characterization of metal sulphide particles, as well as for studying the stability and consequently the aggregation and deposition phenomena of these sulphides.

EXPERIMENTAL

Materials

The samples used were polydisperse, irregular (as has been shown by TEM pictures and laser particle size measurements) colloidal particles of the mixed sulphides $Cu_xZn_{(1-x)}S$ (with x = 0.1, 0.2 and 0.5) provided by Dr. Dalas. FT-IR spectroscopy and X-ray diffraction methods gave the stoichiometry of the sulphides. The number average diameters of the $Cu_{0.1}Zn_{0.9}S$, $Cu_{0.2}Zn_{0.8}S$ and $Cu_{0.5}Zn_{0.5}S$ samples, as they were measured by a laser equipment, were found $(7.56 \pm 1.83)\mu m$, $(5.74 \pm 1.59)\mu m$ and $(6.02 \pm 1.91)\mu m$, respectively.

The suspending medium was triply distilled water containing various volumes of a low foaming, low alkalinity, phosphate, chromate and silicate-free detergent FL-70 (Fisher Scientific Co.) with a pH ranging between 9.0 and 10.5, and 0.02% by weight sodium azide (Fluka AG) as bacteriocide. The FL-70 solution is an uncharacterized mixture of ionic and non-ionic surfactants. For the study of the influence of the detergent nature on the sulphides' size two other surfactants were used: The non-ionic Triton X-100 (iso-octylphenoxypolyethoxyethanol) from BDH with a pH of 6.5 in 1% solution and the uncharacterized Decon-90 from Decon Laboratories Ltd with a pH of 10.1 in 0.05% solution.

For the pH adjustment various surfactants, as well as various concentrations of the same surfactant were added to the suspending medium, while for the variation of the solution ionic strength various amounts of the electrolyte $KClO_3$ were used.

Apparatus and Procedure

The dimensions of the GFFF system, which has been described in detail elsewhere,[9] were 50.3 cm x 2.0 cm x 0.028 cm. The channel void volume V_o (from the injection inlet to the flow cell), measured by the elution of the non retained sodium benzoate peak, was determined to be 2.80 cm^3.

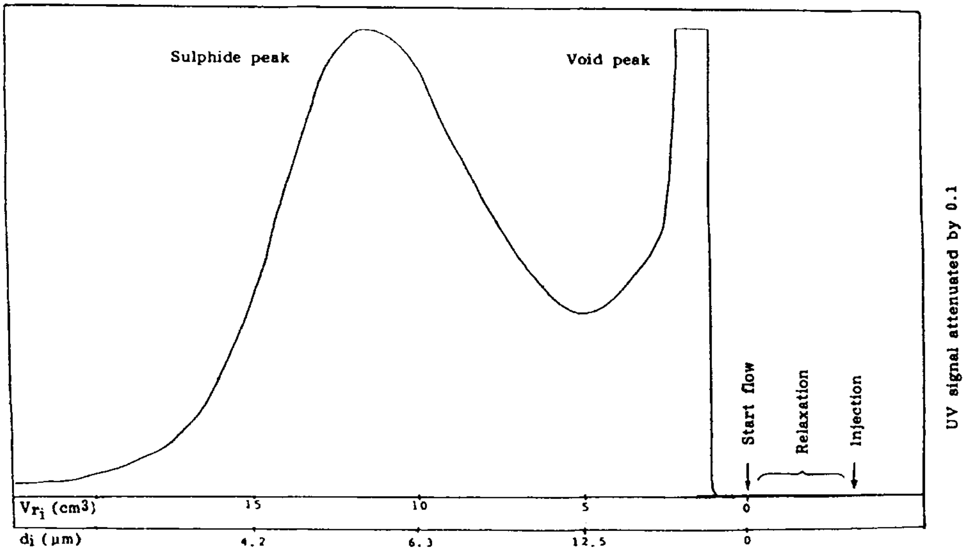

Figure 1. Fractogram and particle diameter scale of the sulphide $Cu_{0.2}Zn_{0.8}S$ obtained by the GFFF technique. Carrier solution: Detergent FL-70 (0.5% v/v)+0.02% (w/w) NaN_3 (pH = 9.4); sample = 25 μL; relaxation time = 10 min; flow rate = 40 $cm^3 h^{-1}$.

The analysis was performed with a Gilson Minipuls 2 peristaltic pump coupled with a Gilson model 111 UV detector operated at 254 nm and a Goerz model RE 541 recorder. All experiments were performed at 25°C.

After 30 min of ultrasound stirring, 25 μL of the sample was injected with a syringe into the channel inlet. The relaxation time was 10 min, while the carrier flow rate varied between 35 and 43 cm^3h^{-1}. The obtained fractograms had the form of Fig. 1.

The electrophoretic mobilities of the sulfide particles were measured in a microelectrophoresis apparatus (Rank, Mark II) by using a four-electrode capillary cell.

The velocities of at least twenty particles in each direction of the electric field were measured at the two stationary layers with an accuracy of ± 10%. The pH of the colloidal suspensions was measured by using a combination glass-saturated calomel electrode (Metrohm).

For the identification of the particular sulphide prepared, a Phillips model PW 1130/00 X-ray diffractometer and a Perkin Elmer 16PC FT-IR spectrophotometer were used, while for the conversion of the measured in GFFF retention volume to particle size, the number average diameters of the three sulphides $Cu_{0.1}Zn_{0.9}S$, $Cu_{0.2}Zn_{0.8}S$ and $Cu_{0.5}$ $Zn_{0.5}S$ were measured by the Spectrex ILI-1000 laser counter.

RESULTS AND DISCUSSION

Determination of Particle Size

The diameter of a spherical particle, d_i, in GFFF, assuming the absence of interactions between the sulphide particles, as well as between the sample particles and the glass column material, is given by the relation:[9]

$$d_i = \left(\frac{V_o}{V_{r_i}}\right) . \frac{w}{3\gamma} = \frac{\lambda}{V_{r_i}} \tag{1}$$

where V_{ri} is the retention volume, w is the channel thickness, γ is a dimensionless factor which represents the complication of lift forces and related hydrodynamic effects,[11] and $\lambda = V_o w / 3\gamma (\mathrm{cm}^4)$.

For polydisperse samples, as it is the case here, the d_i expresses the Stokes diameter, from which the number average, d_N, and weight average, d_w, particle diameters can be determined by the known procedure described elsewhere:[13]

$$d_N = \frac{\sum_i d_i N_i}{\sum_i N_i} = \frac{\lambda \left[\sum_i N_i / V_{r_i} \right]}{\sum_i N_i} \tag{2}$$

$$d_w = \frac{\sum_i d_i S_i}{\sum_i S_i} = \frac{\lambda \left[\sum_i S_i / V_{r_i} \right]}{S} \tag{3}$$

where N_i is the number of particles with constant diameter d_i, S_i is the area under the elution curve of the N_i particles having constant diameter d_i, which is proportional to the weight of the N_i particles and S is the total area of the whole eluted particles.

The parameter λ is computed from Equation (2) using the mean value of d_N found from laser counter measurements for the three sulphides used, together with the values of V_{ri} and N_i obtained from the fractogram. Thus with the aid of the GFFF technique the d_N and d_w values for the polydisperse sulphide samples $Cu_{0.1}Zn_{0.9}S$ (S1), $Cu_{0.2}Zn_{0.8}S$ (S2) and $Cu_{0.5}Zn_{0.5}S$ (S3) can be determined at various experimental conditions using Equations (2) and (3) with $\lambda_{S1} = 6.63 \times 10^{-3}$ cm^4, $\lambda_{S2} = 6.55 \times 10^{-3}$ cm^4 and $\lambda_{S3} = 8.43 \times 10^{-3}$ cm^4.

Variation of Particle Size with the Solution Ionic Strength

The net potential energy of interaction between the sulphide particles, as well as between the sulphide particles and the glass wall material depends on the effective Hamaker constant, the surface potential of the particles and the wall, and of the electrolyte concentration.[7] Variation of the electrolyte concentration, by adding to the suspending medium various amounts of the indifferent electrolyte $KClO_3$, resulted in a variation of the number average and the weight average particle diameter of the sulphide $Cu_{0.1}Zn_{0.9}S$ shown in Fig.2. Although it is well known that an increase in the solution ionic strength generally leads to an increase in particle diameter, our results show an inverse behaviour and the particle size decreases as the ionic strength increases, due to the fact that the interactions between the sulphide particles and the glass wall are stronger than those emerging between the sample particles, which could lead to particles' coagulation.

This is explained in terms of double-layer repulsion between the solute particles and the column material (glass). At low ionic strengths the thickness of the inaccessible region increases and the interactions between the colloidal particles and the column material are negligible. On the other hand, at high ionic strengths the particles are loosely adsorbed into a secondary minimum caused by the combined action of weak double-layer repulsion and strong van der Waals attraction. This explains why sulphide particles in a carrier of high ionic strength have a larger retention time than in a carrier of low ionic strength and consequently a smaller particle size, since, as Equation (1) shows, the particle diameter is inversely proportional to retention time.

Fig.2 shows that the obtained by GFFF particle size is close to that found by the laser counter at ionic strengths lower than 10^{-5} M, while at ionic strengths higher than 10^{-3}M the particle size is kept almost constant. The latter indicates that the attraction potential energy between the sulphide particles and the wall material increases with the electrolyte concentration in the range from

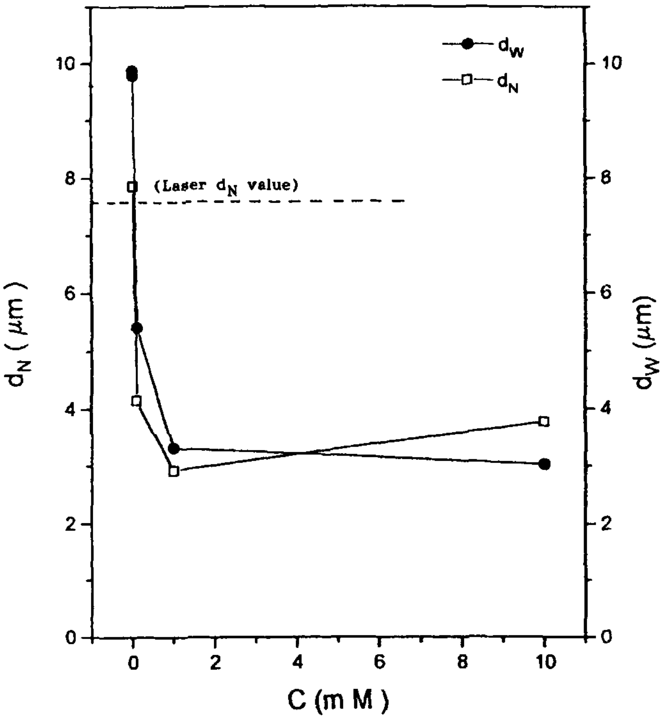

Figure 2. Variation of number and weight average particle diameter for the sulphide $Cu_{0.1}Zn_{0.9}S$ with the ionic strength of the carrier solution, which was adjusted by the electrolyte $KClO_3$. The rest conditions are the same as those in Fig.1.

10^{-5} M to 10^{-3} M, then it is being kept constant. A detailed study of this variation should lead to the determination of the attraction potential energy between the sulphide particles and the glass wall, and consequently between the sulphide particles and whichever solid surface, which is an object of high technological importance.

Variation of Particle Size with the Solution pH

The variation of the solution pH was succeeded either by changing the kind of surfactant (cf. Fig.3 for the sample $Cu_{0.5}Zn_{0.5}S$) or by changing the concentration of the detergent FL-70 (cf. Figs.4a and 4b for the samples $Cu_{0.1}Zn_{0.9}S$ and $Cu_{0.2}Zn_{0.8}S$, respectively). In the first case in which the variation of the pH suspension covers a relatively broad area (between 6.5 and 10.1), the number and weight average diameters of the $Cu_{0.5}Zn_{0.5}S$ particles

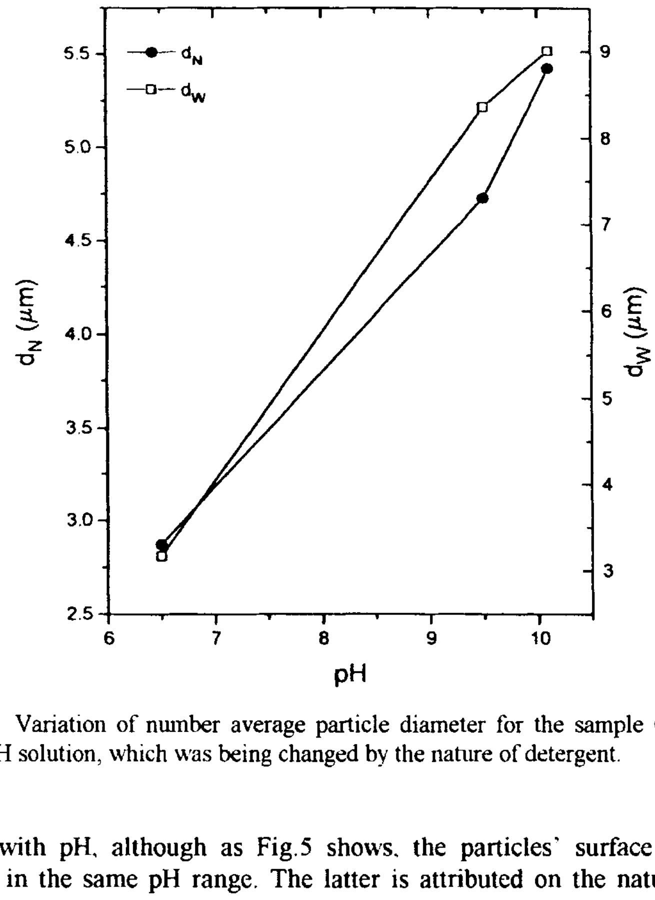

Figure 3. Variation of number average particle diameter for the sample $Cu_{0.5}Zn_{0.5}S$ with the pH solution, which was being changed by the nature of detergent.

increase with pH, although as Fig.5 shows, the particles' surface potential increases in the same pH range. The latter is attributed on the nature of the surfactant rather than on the pH solution.

Comparison of the d_N values determined by the GFFF technique, which are given in Table 1, with that found by laser counter measurements shows that the most suitable from the three used detergents are the alkaline Decon-90 and FL-70 minimizing the interactions between the sulphide particles, as well as those between the sulphide particles and the glass column material. But one must bear in mind that the conversion parameter λ was computed using carrier solution with the detergent FL-70, thus making the above comparison precarious. For this reason, we compare the polydispersity factors $\xi = d_w/d_N$ for the sample $Cu_{0.5}Zn_{0.5}S$ obtained by the GFFF technique using three different surfactants. Due to the fact that the sample is identical in all three surfactants the parameter ξ given in Table 1 is a measure also of the sample's degree of aggregation. Thus the aggregation rate increases from the Triton X-100 to

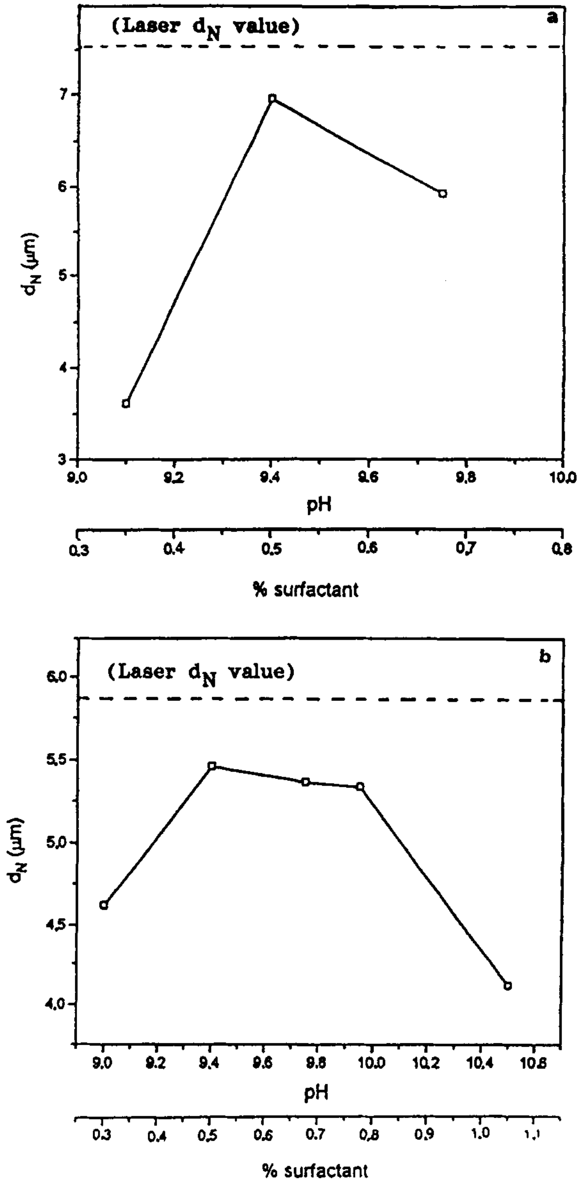

Figure 4. The dependence of number average particle diameter on the solution pH, which was being varied by the surfactant concentration. (a) Sample $Cu_{0.1}Zn_{0.9}S$; (b) Sample $Cu_{0.2}Zn_{0.8}S$.

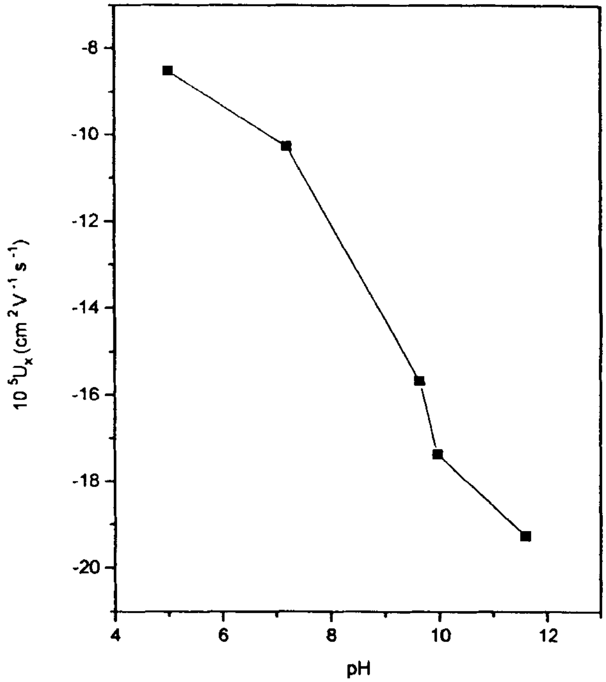

Figure 5. The dependence of the electrophoretic mobility, U_X, of the sample $Cu_{0.5}Zn_{0.5}S$ on the suspension pH.

Table 1

Number Average, d_N, and Weight Average, d_W, Particle Diameters for the $Cu_{0.5}Zn_{0.5}S$ Sulphide Sample Obtained by the GFFF Technique with Three Different Surfactants, as well as Corresponding Polydispersity Factors, ξ.

Detergent	pH	d_N(μm)	d_W(μm)	$\xi = d_W/d_N$
Triton X-100	6.5	2.81	3.30	1.17
FL-70	9.4	5.22	7.30	1.40
Decon-90	10.1	5.52	8.80	1.59
Laser Counter	---	6.02	---	---

FL-70 and then to Decon-90 indicating that the most suitable detergent minimizing the aggregation process for the sample $Cu_{0.5}Zn_{0.5}S$ is the non-ionic Triton X-100. The addition of the non-ionic Triton X-100 surfactant to the sulphide sample, whose particles carry a small negative charge, increased the stability of the dispersion to flocculation. The high stability of the sample is due to the adsorption of the non-ionic surfactant onto the sulphide particles.

In the second case, the variation of d_N with the solution pH in both samples appears a maximum at the pH value 9.4 corresponding to the detergent FL-70 concentration of about 0.5% v/v. The maximum d_N values for both samples are those approaching the d_N values found by laser counter measurements. The latter indicates that the ideal detergent concentration for minimizing the interactions between the sulphide particles and the glass column material and, consequently, that which is minimizing the deposition phenomena of the sulphide particles at the glass substrate, is that of about 0.5% by volume FL-70.

The decreased particle size at lower than 0.5% by volume concentrations of surfactant is attributed to the decrease of the surface potentials, as Figs.6a and 6b show, which leads to an increase in the attraction potential energy between the sulphide particles and the glass substrate. As a consequence an increase of the retention volume and a decrease of the particle diameter is observed.

The decreased particle size at higher than 0.5% by volume concentrations of surfactant, although the zeta potentials continued to become more negative, as Figs. 6a and 6b show, can be attributed either to the compression of the electrical double-layer by the increased surfactant concentration, which leads to an increase in the potential energy of attraction between the sulphide particles and the glass column or to the increase of the effective Hamaker constant A_{132}, which leads also to an increase of the attraction potential energy, U_A, between the particles and the wall.

The latter can be explained as follows: The surfactants, as it is well known, reduce the surface tension γ_{33} of the suspended medium, and consequently the Hamaker constant A_{33}, since:[16]

$$A_{33} \approx 2.1 \times 10^{-21} \gamma_{33} \qquad (4)$$

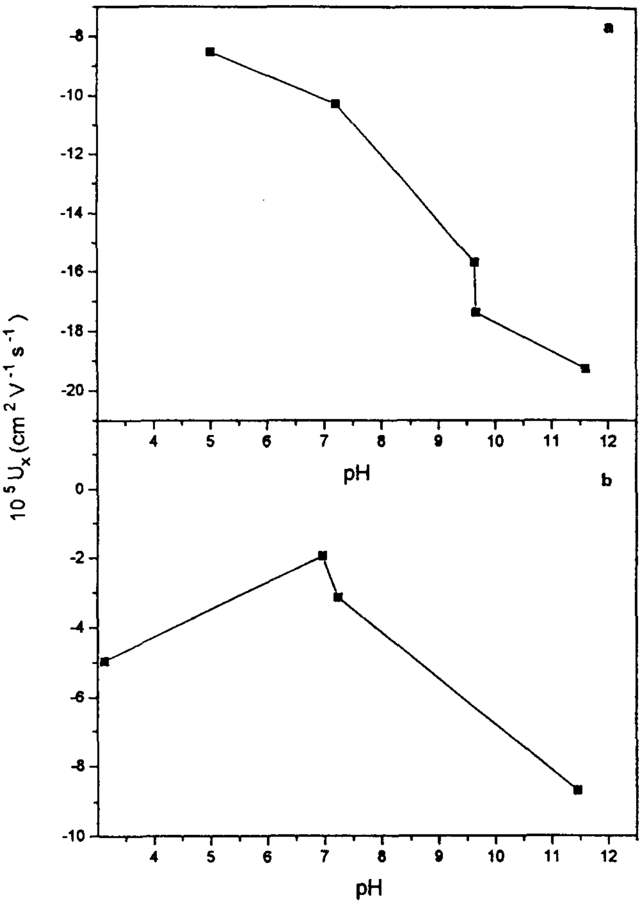

Figure 6. Variation of the electrophoretic mobility with the pH solution for the samples $Cu_{0.1}Zn_{0.9}S$ (a) and $Cu_{0.2}Zn_{0.8}S$ (b).

where γ_{33} is in mJ.m^{-2} and A_{33} in J. The effective Hamaker constant, A_{132}, between the sulphide particles and the channel wall material in the presence of a medium is related with the Hamaker constants of the sample (A_{11}), the wall material (A_{22}) and the medium (A_{33}), via the equation:

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \quad (5)$$

Equation (5) shows that a decrease in the medium Hamaker constant A_{33} caused by an increase in the surfactant concentration leads to an increase in the effective Hamaker constant A_{132}-supposing that both A_{11} and A_{22} are independent of the surfactant concentration- and consequently to an increase in the attraction potential energy, since:[16]

$$U_A = -\frac{A_{132}}{12\pi} l^{-2} \tag{6}$$

where l is the distance between the particles and the wall. In order to investigate whether the ionic strength or the effective Hamaker constant is the main factor affecting the interaction between the sulphide particles and the glass wall an experiment was performed with a carrier containing the surfactant FL-70 (0.5% v/v) and 10^{-3}M $KClO_3$ thereby varying its ionic strength (the A_{33} parameter is supposed to be kept constant in both carriers).

The obtained particle size is almost identical with that found with a suspending medium containing only the detergent FL-70 indicating that the variation of particle size with the surfactant concentration in that particular range should be attributed on the variation of the effective Hamaker constant rather than on the variation of the solution ionic strength.

It must be pointed out that the variation of the pH solution by adding different amounts of acids or bases, which presented in another work,[17] led (i) to the total adhesion of the $Cu_{0.1}Zn_{0.9}S$ particles at the glass channel wall at pH<7.5, (ii) to the partial adhesion of the same particles at the pH range between 7.5 and 9.0, and (iii) to the total elution of the suspended particles at pH higher than 9.0.

Variation of Particle Size with Time

The variation of number average and weight average diameter of the sulphide $Cu_{0.5}Zn_{0.5}S$ particles with time is shown in Fig.7. Contrary to the expected increase of the d_N and d_w values with time, due to possible aggregation, the particle diameters decrease with time, which means that the retention time increases with time. This should be attributed either to the increase of the interaction forces between the sulphide particles and the glass substrate, responsible for the slow movement of the particles along the column or to the "true" decrease of particle size with the agitation time. All the factors affecting the interaction forces between the particles and the wall are kept constant during the whole working time indicating that true particle's size

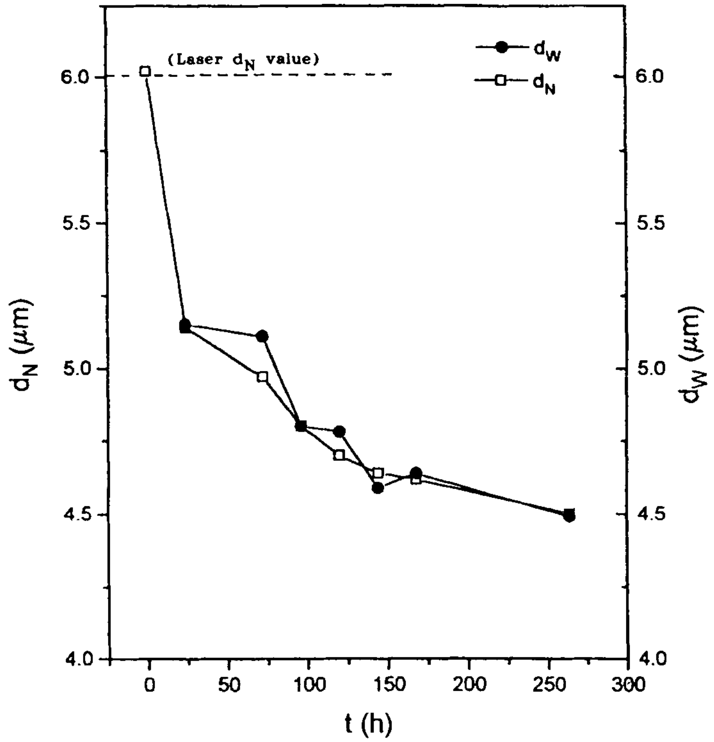

Figure 7. The dependence of number average particle diameter for the sample $Cu_{0.5}Zn_{0.5}S$ on the agitation time.

variation occurs with time. The stability of particle size at times greater than about 140 h (≈ 6 days) indicates that, before use, one should agitate these particular samples for a time interval of about six days. All of our experiments were performed with a constant agitation time of about 30 minfor all of the samples, thus making worthy all the presented comparisons.

CONCLUSION

From the data presented, it can be concluded that the ideal carrier solutions for minimizing coagulation and adhesion phenomena in studying sulphide samples by GFFF are those containing (i) between the surfactants FL-70, Decon-90 and Triton X-100 the non-ionic Triton X-100, (ii) between the concentrations of the FL-70 surfactant that of about 0.5% v/v, (iii) between the concentrations of the indifferent electrolyte $KClO_3$ those which are lower than 10^{-5}M, and (iv) between the pH values of the suspended medium those which are higher than 9.0 and particularly that of 9.4 containing 0.5% v/v of the detergent FL-70.

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